

**WHAT IS CLAIMED IS:**

1. A monovinylarene/conjugated diene block copolymer, comprising:  
5 a random (conjugated diene<sub>x</sub>/monovinylarene<sub>y</sub>)<sub>m</sub> block, wherein x is about 2.5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5 wt% to 100 wt%; and  
a (conjugated diene)<sub>n</sub> block;  
wherein n is from about 20 wt% to about 30 wt%, m is from about 70 wt% to about 80 wt%, and m + n is from about 90 wt% to 100 wt%.  
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2. The monovinylarene/conjugated diene block copolymer of claim 1, wherein x is about 5 wt% to about 10 wt%.
- 15 3. The monovinylarene/conjugated diene block copolymer of claim 1, wherein y is about 90 wt% to about 95 wt%.
4. The monovinylarene/conjugated diene block copolymer of claim 1, wherein n is about 25 wt% and m is about 75 wt%.
- 20 5. The monovinylarene/conjugated diene block copolymer of claim 1, wherein the T<sub>g</sub> is at least about 10°C less than the T<sub>g</sub> of a reference polymer differing only in x being about 0 wt% and y being about 100 wt%.
- 25 6. The monovinylarene/conjugated diene block copolymer of claim 5, wherein the T<sub>g</sub> is at least about 20°C less than the T<sub>g</sub> of the reference polymer.
7. The monovinylarene/conjugated diene block copolymer of claim 6, wherein the T<sub>g</sub> is at least about 30°C less than the T<sub>g</sub> of the reference polymer.

8. The monovinylarene/conjugated diene block copolymer of claim 1, further comprising a monovinylarene/conjugated diene block.
9. The monovinylarene/conjugated diene block copolymer of claim 1, further comprising a monovinylarene block.
10. An article, comprising the monovinylarene/conjugated diene block copolymer of claim 1.
11. The article of claim 10, wherein the article is a shrink film.
12. A method of preparing a monovinylarene/conjugated diene block copolymer having a low  $T_g$ , comprising:
  - (a) charging a monovinylarene monomer, a conjugated diene monomer, an initiator, and a randomizer, allowing polymerizing to occur, to produce a random (conjugated diene<sub>x</sub>/monovinylarene<sub>y</sub>)<sub>m</sub> block;
  - (b) charging a monovinylarene monomer, a conjugated diene monomer, and an initiator, allowing polymerization to occur, to produce a monovinylarene/conjugated diene block;
  - (c) charging a conjugated diene monomer, and allowing polymerization to occur, to produce a (conjugated diene)<sub>n</sub> block; and
  - (c) charging the reaction mixture with a coupling agent, to form monovinylarene/conjugated diene block copolymer.
13. The method of claim 12, wherein x is about 2.5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5 wt% to 100 wt%.
14. The method of claim 12, wherein n is from about 20 wt% to about 30 wt%, m is from about 70 wt% to about 80 wt%, and m + n is from about 90 wt% to 100 wt%.

15. A monovinylarene/conjugated diene block copolymer, produced according to the method of claim 12.

16. A method of preparing a monovinylarene/conjugated diene block copolymer  
5 having a low  $T_g$ , comprising:

(a) charging an initiator and a monovinylarene monomer and allowing polymerization to occur, to produce a monovinylarene block;  
10 (b) charging a randomizer, an initiator, and a conjugated diene/monovinylarene monomer mixture and allowing polymerization to occur, to produce a random (conjugated diene<sub>x</sub>/monovinylarene<sub>y</sub>)<sub>m</sub> block;

15 (c) charging a conjugated diene monomer and allowing polymerization to occur, to produce a conjugated diene block;

(d) charging a randomizer, an initiator, and a conjugated diene/monovinylarene monomer mixture and allowing polymerization to occur, to produce a random (conjugated diene<sub>x</sub>/monovinylarene<sub>y</sub>)<sub>m</sub> block;

20 (e) charging a conjugated diene monomer and allowing polymerization to occur, to produce a conjugated diene block; and

(f) charging the reaction mixture with a coupling agent, to form monovinylarene/conjugated diene block copolymer.

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17. A monovinylarene/conjugated diene block copolymer, produced according to the method of claim 16.

18. A method of fabricating an article, comprising:

25 forming a monovinylarene/conjugated diene block copolymer into the article, wherein the monovinylarene/conjugated diene block copolymer comprises (i) a random (conjugated diene<sub>x</sub>/monovinylarene<sub>y</sub>)<sub>m</sub> block, wherein x is about 2.5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5 wt% to 100 wt%; and (ii) a (conjugated diene)<sub>n</sub> block; wherein n is from about 20 wt% to about 30

wt%, m is from about 70 wt% to about 80 wt%, and m + n is from about 90 wt% to 100 wt%.

19. The method of claim 18, wherein forming comprises sheet extrusion, 5 thermoforming, injection molding, blow molding, film blowing, or film casting.
20. A monovinylarene/conjugated diene block copolymer, comprising the structure: (B/S)-B-CA,  
wherein (B/S) is a random monovinylarene/conjugated diene block; B is a 10 conjugated diene block; CA is a coupling agent residue; and - is a covalent linkage between blocks.
21. The monovinylarene/conjugated diene block copolymer of claim 20, further comprising a second (B/S) block covalently linked to the (B/S) block of the (B/S)-B-CA 15 structure.
22. The monovinylarene/conjugated diene block copolymer of claim 20, further comprising a second (B/S)-(B/S)-B structure covalently linked to the (B/S) block of the (B/S)-B-CA structure. 20
23. The monovinylarene/conjugated diene block copolymer of claim 20, further comprising a second (B/S)-B structure covalently linked to the (B/S) block of the (B/S)-B-CA structure.
24. The monovinylarene/conjugated diene block copolymer of claim 20, further comprising a second S-(B/S)-B- structure covalently linked to the (B/S) block of the (B/S)-B-CA structure, wherein S is a monovinylarene block. 25
25. A monovinylarene/conjugated diene block copolymer, comprising the structure: 30 <B/S>2-<B/S>3-<B/S>4-<B/S>5-CA,

wherein  $\langle B/S \rangle$  is a tapered monovinylarene/conjugated diene block;  $\langle B/S \rangle 2$  has a conjugated diene content from about 2.5 wt% to about 10 wt%, and  $\langle B/S \rangle 3$ ,  $\langle B/S \rangle 4$ , and  $\langle B/S \rangle 5$  have a conjugated diene content from about 30 wt% to about 70 wt%.

5 26. The monovinylarene/conjugated diene block copolymer of claim 25, further comprising a  $\langle B/S \rangle 1$  block covalently linked to the  $\langle B/S \rangle 2$  block of the  $\langle B/S \rangle 2$ - $\langle B/S \rangle 3$ - $\langle B/S \rangle 4$ - $\langle B/S \rangle 5$ -CA structure, wherein  $\langle B/S \rangle 1$  has a conjugated diene content from about 2.5 wt% to about 10 wt%.

10 27. A monovinylarene/conjugated diene block copolymer, comprising the structure:  $(B/S)_1-(B/S)_2-\langle B/S \rangle_3-\langle B/S \rangle_4-\langle B/S \rangle_5$ -CA,  
wherein  $(B/S)$  is a random monovinylarene/conjugated diene block;  $\langle B/S \rangle$  is a tapered monovinylarene/conjugated diene block; CA is a coupling agent residue; - is a covalent linkage between blocks;  $(B/S)_1$  and  $(B/S)_2$  each have a conjugated diene content from about 2.5 wt% to about 10 wt%; and  $\langle B/S \rangle_3$ ,  $\langle B/S \rangle_4$ , and  $\langle B/S \rangle_5$  each have a conjugated diene content from about 30 wt% to about 70 wt%.

15 28. A monovinylarene/conjugated diene block copolymer, comprising the structure:  $(B/S)_1-(B/S)_2-(B/S)_3-(B/S)_4-(B/S)_5$ -CA,  
wherein  $(B/S)$  is a random monovinylarene/conjugated diene block; CA is a coupling agent residue; - is a covalent linkage between blocks;  $(B/S)_1$  and  $(B/S)_2$  each have a conjugated diene content from about 2.5 wt% to about 10 wt%; and  $(B/S)_3$ ,  $(B/S)_4$ , and  $(B/S)_5$  each have a conjugated diene content from about 30 wt% to about 70 wt%.